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HYDROXYAPATITE-WOLLASTONITE BIOCERAMICS

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The results of research and development of bioceramic materials based on calcium hydroxyapatite (HA) and natural mineral wollastonite are reported. The process of production of HA by several reactions is investigated. The optimum bioceramic compositions for medical purposes are determined.

Ceramic materials for medical application have recently acquired great significance. Bioceramics are composite materials combining properties needed for medical applications: biological activity and sufficient mechanical strength. Bioceramic materials are used for production of artificial teeth, bones, and articulations. The main requirements imposed upon such materials are biocompatibility with the living organism and high chemical purity. The mineral basis of the human bone is the compound $Ca_5(PO_4)_3OH$, whose natural analog is the mineral hydroxyapatite (HA). Natural HA does not satisfy the medical standard of chemical purity, and for the same reason HA obtained from animal bones cannot be used without sophisticated preliminary purification.

The published data on HA properties depending on reaction schemes and production technologies are contradictory [1 – 4]. Therefore, studies in the field of the synthesis of artificial HA with the aim of optimization of its technology and reproducibility of results are topical problems.

The synthesis of HA can be performed according to several reactions, which can be split into two groups: liquid-phase and solid-phase synthesis. The present study considered the process of HA production based on three reactions:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O; \quad (1)$$

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3; \quad (2)$$

$$10CaCO_3 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 10CO_2 + 12NH_3 + 8H_2O. \quad (3)$$

In studying schemes (1) and (2) of liquid-phase synthesis, the variable parameters were the ratio Ca : P ranging from 1.00 to 1.75, the stoichiometric ratio being equal to 1.67, and the duration of precipitate aging. The obtained HA samples were studied using integrated thermal analysis and IR-spectroscopic and x-ray phase analysis. The solution-based synthesis resulted in a polyphase product with a predominance of tricalcium phosphate $Ca_3(PO_4)_2$ both immediately after drying and after firing. Moreover, to produce HA powder with acceptable technological properties, its preliminary calcination is required anyway.

In the synthesis of single-phase HA using the solid-phase method according to reaction (3), of special significance is a strict correspondence of the initial mixture to the stoichiometric composition (Ca : P = 1.66(6)) [5].

The homogenization of mixtures was carried out in ethyl alcohol in a planetary mill. Firing was carried out in silite furnaces in platinum crucibles at 900, 1000, 1100, and 1200°C; the duration of exposure at the final temperature was 2 h. Studies of the reaction product using complex thermal, x-ray phase, and IR-spectroscopic analysis methods indicate that HA with the ratio Ca : P = 1.66(6) obtained in solid-phase synthesis, which is produced at firing temperature 1100°C and is the closest to the single-phase state, has the optimum properties for its further application in the production of pure hydroxyapatite ceramics or composite materials. The firing temperatures 900 and 1000°C were not sufficient to complete the process of HA synthesis. The samples fired at 1200°C had a lower sintering capacity.

Figure 1 represents the IR spectra of HA produced by the liquid-phase method with the ratio Ca : P = 1.67 and precipitate aging duration of 48 h and HA obtained by the solid-phase method at the firing temperature 1100°C. The IR spectra are typical for tetrahedral oxygen-containing anions, in particular, PO_4^{3-}. The presence of the OH group in HA is manifested by an intense absorption band with a frequency of about 3600 cm^{-1} [6]. The IR spectrum of solid-phase HA does not have an absorption band with a frequency of 800 cm^{-1} characterizing the presence of an OH group, which presumably belongs to adsorbed water.

Thus, liquid-phase reactions are very sensitive to the conditions of synthesis, and their results have low repro-

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ducibility. The solid-phase scheme of HA synthesis is preferable. In both case, chemically pure reactants should be used for HA synthesis.

World practice indicates that the use of HA without additives for implant production is not efficient, due to its low strength parameters. Researchers are studying the effect of the doping additives Y_2O_3 and ZrO_2, with the aim of improving the strength of hydroxyapatite ceramics [2]. Bioceramics are also represented by composite materials made of HA and synthesized or extra-pure natural minerals which impart specific properties (strength, porosity, etc.). Apatite-wollastonite composites are extensively used in world practice for the production of bioglass ceramics [7].

For the purposes of the present study the natural wollastonite $CaSiO_3$ from the Slyudyanskoe deposit (Irkutsk Region) was used as the wollastonite component. The above material is known for a high content of the main mineral and a low impurity content, which makes it possible to apply it for medical purposes. The application of extra-pure natural materials makes it possible to reduce the cost of implant production. Furthermore, as distinct from synthesized materials, natural wollastonite has a clearly expressed needle-shaped habitus with a ratio between the needle length and their diameter equal to 15 – 20 or more. This will presumably facilitate the production of interwoven reinforcing mesh of wollastonite needles in the implant. With the shortage of the highly disperse component, mainly HA, this makes it possible to obtain a highly porous structure with through pores.

The highest porosity is shown by the materials containing single-fraction wollastonite, and the pore size depends on the crystal size. The study of porosity is important to ensure the assimilation of bioceramics and their intergrowth with bone tissues. The present study considers wollastonite of two fractions: $N_1 < 0.15$ mm and $0.3 < N_2 < 0.5$ mm.

The chemical compositions of the materials and ceramic mixtures are shown in Tables 1 and 2. The compositions selected to study the regularities of the formation of structure and properties in bioceramics had a variable ratio HA : wollastonite with a step of 10%. In order to decrease the firing temperature, feldspar (melting temperature 1120 – 1150°C) in an amount of 5% (above 100%) was introduced to the mixtures. For a comparative study of the effect of feldspar on ceramic properties, the same series of compositions was studied without adding feldspar.

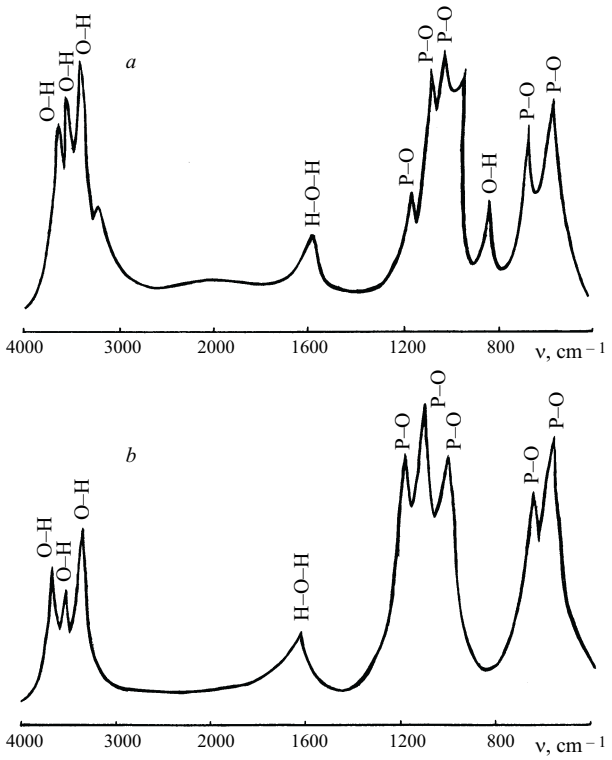

Fig. 1. IR spectra of HA produced by liquid-phase (*a*) and solid-phase (*b*) methods.

In order to study the sinterability and the properties of ceramics, cylindrical samples were molded and fired at tem-

TABLE 1

Component	Weight content, %									
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	H_2O
Hydroxyapatite	–	–	–	–	55.78	–	–	–	42.43	1.79
Wollastonite	51.70	0.61	–	–	46.37	0.98	0.22	–	0.12	–
Feldspar	66.50	18.35	0.13	0.10	0.51	0.19	11.72	2.50	–	–

TABLE 2

Component	Weight content in mixture, %											
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9	M_{10}	M_{11}	M_{12}
Hydroxyapatite	10	10	30	30	40	40	100	100	50	50	0	0
Wollastonite:												
N_1	–	–	–	–	–	–	0	0	50	50	100	100
N_2	90	90	70	70	60	60	–	–	–	–	–	–
Feldspar	0	5	0	5	0	5	0	5	0	5	0	5

TABLE 3

Mixture	Porosity, %	Strength, MPa		Bioactivity, %	Mean effective pore diameter, μm
		compressive	bending		
M_1	60	–	10	75	260
M_2	54	–	19	70	230
M_3	52	–	14	84	250
M_4	45	–	32	80	210
M_5	38	–	19	90	180
M_6	30	–	36	87	110
M_7	0.5	317	102	–	–
M_8	0.3	309	95	–	–
M_9	0.1	385	119	–	–
M_{10}	0	389	124	–	–
M_{11}	0.7	364	110	–	–
M_{12}	0	371	106	–	–

peratures from 1125 to 1250°C with an interval of 25°C. In the sintered samples with wollastonite of the N_2 fraction, the porosity, the bending strength, the biological activity, and the mean effective pore diameter were determined, and furthermore, the porosity and the compressive and bending strength were determined for the sintered samples with wollastonite of the N_1 fraction. The measurement results are shown in Table 3.

Mixtures $M_1 - M_6$ exhibit good porosity and high biological activity. With the HA content below 10%, the bioactivity of the ceramic decreases, and with the HA content above 40%, the porosity decreases. The bioactivity of the materials was estimated by the relative surface area (%) of the implant intergrowth with the bone (RF Patent No. 2105529). The mixtures with wollastonite of fraction N_2 ($M_7 - M_{12}$) have virtually zero porosity. Such compact structure determines the high mechanical strength of the material. Feldspar, which is the main glass-forming component, primarily reacts with finely disperse HA, which decreases the melt viscosity. The bioactivity of the resulting vitreous phase is determined by its content of P_2O_5. The introduction of more than 10% feldspar to the mixture significantly decreases the porosity of the material.

Figure 2 shows the x-ray diffraction patterns of mixtures M_7, M_{10}, and M_{11}. Two phases are registered in mixture M_{10}: HA and wollastonite. This is evidence of the fact that in liquid-phase sintering accompanied by increase in the melt content up to 30 – 50%, no predominant dissolution of a particular phase takes place, and new crystalline phases are not crystallized in the course of melt cooling. Correlating this fact with the significant strength of ceramic samples, one can assume with a great degree of probability that wollastonite and HA released from the melt mostly crystallize on the existent wollastonite needles and HA particles, thus reinforcing the macrostructural lattice of the crystal phases (the skeleton). The x-ray diffraction patterns of mixtures M_7 and M_{11} correlate with pure HA and pure wollastonite, respectively.

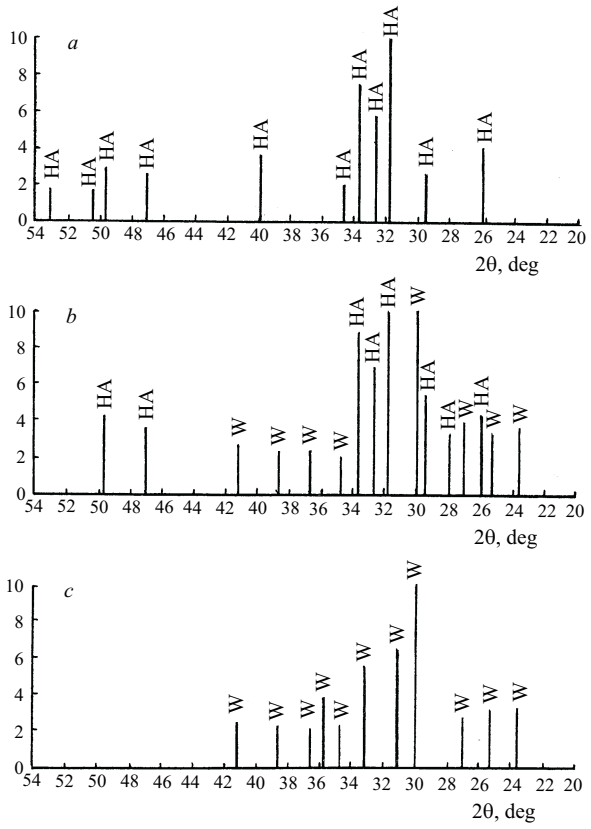

Fig. 2. X-ray diffraction patterns of bioceramic samples of compositions M_7 (*a*), M_{10} (*b*), and M_{11} (*c*): HA) hydroxyapatite; W) wollastonite.

The best for biomedical applications among the porous bioceramic materials ($M_1 - M_6$) are compositions M_3 and M_4, which have good porosity and bioactivity. The introduction of feldspar to the mixture makes it possible to reduce the firing temperature. Dental implant surgery requires compactly sintered bioceramics with high mechanical strength. The most preferable in this respect are mixtures M_9 and M_{10}. The sufficient HA content in these mixtures should ensure high bioactivity of the materials.

Thus, the controlled ratio of the apatite and wollastonite components in ceramic mixtures makes it possible to design bioceramic compositions having specified strength and porosity and, accordingly, the implant resorption time needed for specific medical applications.

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